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Recent work has shown that the range of synthesis of new and useful phos-
phazene derivatives can be dramatically expanded by incorporation of an organo-
functional substituent on the phosphazene ring. This substituent can serve as
the site for various synthetic transformations leading to new monomeric and
polymeric phosphazene moieties. Initial work on propenylphosphazenes and their
copolymerization with organic monomers will be briefly discussed. In addition
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20. $N_3P_3Cl_5OCH=CH_2$ and related compounds have been prepared and characterized. Both homopolymerization and a broad range of copolymerization reactions of $N_3P_3Cl_5OCH=CH_2$ will be presented. The properties of these systems can be modified by reactions of the cyclophosphazene units in the polymer.

Organofunctional Phosphazenes and Organofunctional
Phosphazene Polymers.

by

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Organofunctional Phosphazenes and Organofunctional Phosphazene Polymers

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SYNOPSIS

Recent work has shown that the range of synthesis of new and useful phosphazene derivatives can be dramatically expanded by incorporation of an organofunctional substituent on the phosphazene ring. This substituent can serve as the site for various synthetic transformations leading to new monomeric and polymeric phosphazene moieties. Initial work on propenylphosphazenes and their copolymerization with organic monomers will be briefly reviewed. The synthesis of new improved phosphazene monomers which lead to flame retardant copolymers will be discussed. In addition to electron rich olefins such as alkoxylvinylphosphazenes, novel alkynlphosphazene/styrene copolymers have been prepared. The vinyl alcohol derivative, $N_3P_3Cl_5OCH=CH_2$ and related compounds have been prepared and characterized. Both homopolymerization and a broad range of copolymerization reactions of $N_3P_3Cl_5OCH=CH_2$ will be presented. The properties of these systems can be modified by reactions of the cyclophosphazene units in the polymer.

INTRODUCTION

In this paper we wish to discuss our research concerning the combination of phosphazene and high polymer chemistry. Other groups [1], particularly Allcock and his students [2], are investigating the range and potential of polyphosphazenes. Our approach has been a significantly different one in that we are working on ways to incorporate the cyclophosphazene ring system directly onto a traditional organic polymer matrix. In order to hopefully make clear the nature of our approach and of the chemistry involved, we will present some brief introductory material on phosph----- chemistry followed by an examination of the first organofunctional phosphazenes, the propenylphosphazenes, we explored. The remainder of the discussion will demonstra -

how we have used what we learned in the study of the propenyl system to develop a broad range of new polymer systems.

With apologies to readers who are familiar with phosphazene chemistry, we would like to place phosphazenes in the context of other related systems. There are a variety of inorganic rings based on alternating elements with one set containing nitrogen, oxygen or phosphorus atoms and the other set consists of a broad range of first and second row elements. Certain of these inorganic heterocycles are shown below and monographs are available [3] on the general area.
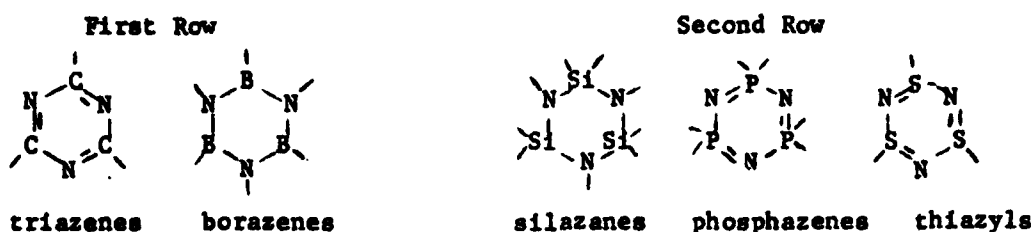
The chemistry of the halocyclophosphazenes is dominated by nucleophilic substitution reactions at the phosphorus centers [4,5]. Some indication of the range of available reactions is given below using the commercially available hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, as an example. Similar reactions occur with the tetrameric and higher membered rings of the series.
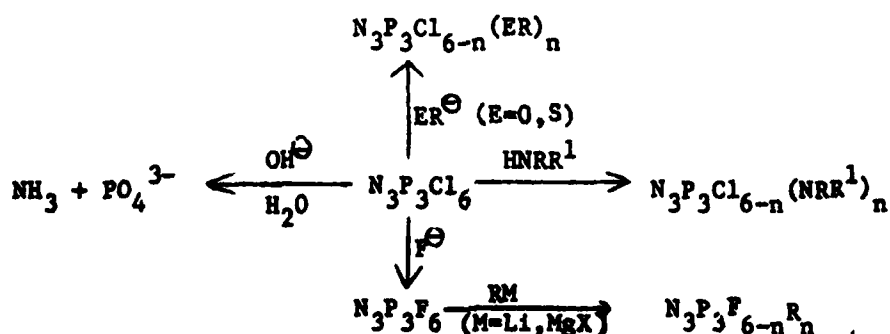
The structural consequence of incomplete substitution is a complex series of isomeric materials. On going from mono to disubstitution, reaction may occur at the substituted phosphorus atom (geminal) or at distant phosphorus atoms (non-geminal). For non-geminal materials, two isomeric forms with substituents cis or trans to each other about the average plane of the ring are possible. The three isomers having the stoichiometry $N_3P_3X_4R_2$ are shown below. Similar isomeric mixtures occur at the tri and tetra stages of substitution.
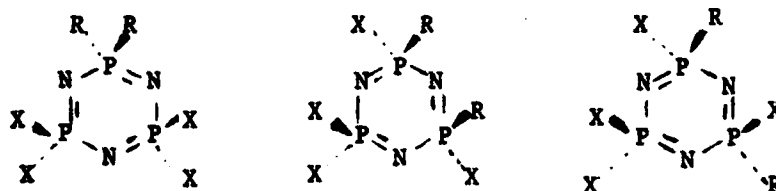
In addition to fundamental chemistry, there has been considerable interest in the applications potential of both cyclic and high polymeric phosphazenes. A brief overview of some of the exciting possibilities along these lines is presented in Table I. As indicated in Table I, our approach initially involved copolymerization of organophsophazenes with traditional organic monomers. In order to effect this sort of reaction, one needs an appropriate reactive site on the phosphorus atom hence our long standing interest in the synthesis of phosphazenes with side chains which can serve as sites for further synthetic transformations. We refer to these materials as organofunctional phosphazenes [11].

PROPENYLPHOSPHAZENES

Given our experience with the synthesis of organophosphazenes [11], the first systems chosen to study were derived from the reactions of both 1 and 2-propenyl lithium with hexafluorocyclotriphosphazene, $N_3P_3F_6$ [13]. The 1-propenyl lithium reactions are relatively clean leading to both the mono and geminally disubstituted

TABLE 1

Applied Phosphazene Chemistry

High Performance Polymers
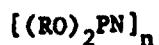
$[(RO)_2PN]_n$ Allcock [2], Firestone ("PNF") [6]

Biomedicinal Agents

$N_3P_3(N])_6$ Labarre [7]

$2,4-N_3P_3Cl_4(NHCH_2CH_2Cl)_2$ Allen [8]
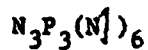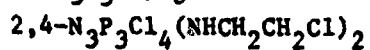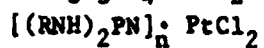
$[(RNH)_2PN]_n \cdot PtCl_2$ Allcock [9]

Fire Retardants

$N_3P_3Cl_6$ Additive [4,5]
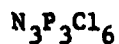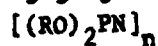
$[(RO)_2PN]_n$ Fire Retardant Polymer [1]

Copolymerization with Organic Monomers   Allen [10,11]

$$N_3P_3F_6 \xrightarrow{\text{LiCH=CHCH}_3} N_3P_3F_5CH=CHCH_3 \xrightarrow{\text{LiCH=CHCH}_3} 2,2\text{-}N_3P_3F_4(CH=CHCH_3)_2$$

$$N_3P_3F_6 \xrightarrow{\text{LiC(CH}_3)=CH_2} N_3P_3F_5C(CH_3)=CH_2 \quad (\underset{\sim}{1}) \xrightarrow{\text{LiC(CH}_3)=CH_2} \text{degradation products}$$
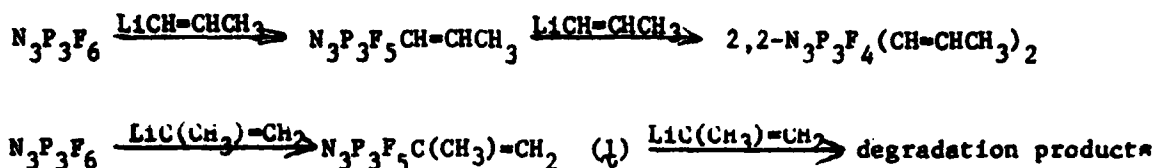
derivatives. The 2-propenyl lithium reactions are of greater interest in that they lead to α-olefins which were expected to be interesting vinyl monomers. One can obtain 2-propenylpentafluorocyclotriphosphazene ($\underset{\sim}{1}$) in modest yields accompanied by a considerable quantity of oily residues. These oils are the only product in all attempts to produce disubstituted 2-propenylphosphazenes. The organofunctional nature of the various propenylphosphazenes was demonstrated by facile bromination and hydrogenation reactions.

We have used $\underset{\sim}{1}$ as our entry point into polymer chemistry [10]. Attempts at radical homopolymerization lead only to traces of oligomers probably due to reactivity and steric problems. Radical copolymerization of $\underset{\sim}{1}$ with styrene (or vinyl benzyl chlorides) produces a broad range of the expected copolymers and thus demonstrating

$$\underset{\sim}{1} + x \quad ClCH_2C_6H_4CH=CH_2 \xrightarrow{R^\cdot} \{(\underset{\underset{C_6H_4CH_2Cl}{|}}{CHCH_2-}) \quad (\underset{\underset{N_3P_3F_5}{|}}{C(CH_3)CH_2})_y\}_n$$

$$x = 0.11 \text{ to } 7.69 \qquad y = .06 \text{ to } 0.62$$

$$\underset{\sim}{1} + x \quad C_6H_5CH=CH_2 \xrightarrow{R^\cdot} \{(\underset{\underset{C_6H_5}{|}}{CHCH_2}) (\underset{\underset{N_3P_3F_5}{|}}{C(CH_3)-CH_2})_y\}_n$$

$$x = 0.11 \text{ to } 4.00 \qquad y = 0.07 \text{ to } 0.58$$
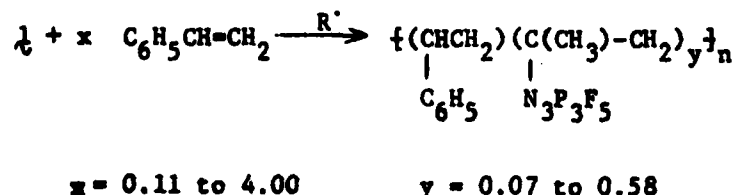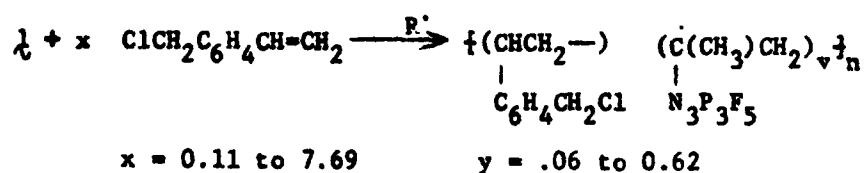
our ability to affix the cyclophosphazene unit to traditional organic polymers. The next question which arose was what sort of property modifications of the parent organic homopolymer are affected by the addition of the inorganic (phosphazene) component. Our most immediate concern was flame retardancy so we were pleased to

note that in simple flame tests the copolymers will not burn nor produce smoke. Copolymers which had been swelled in organic solvents burn in the flame source but self extinguish when the external flame source was removed. We also have noted that the new copolymers, and indeed all others which we have subsequently prepared, exhibited a broad range of solubility reflecting differing solvation abilities of pendant organic and inorganic rings. Initial exploration of thermal stability by TGA indicated that there is actually an increase in the temperature required before 50% weight loss is attained in the copolymer compared to the organic homopolymer. If one heats a copolymer sample on the vacuum line to 250°, physical changes were noted in the sample but volatiles were not observed. Broadening of the phosphorus-nitrogen stretching frequency was noted in the IR spectrum. Thermal degradation in solution results in modest decreases in molecular weight. We are currently investigating the mechanism of thermal decomposition of these materials.

In addition to thermal degradation, we have explored traditional phosphazene reactions as applied to the phosphazene unit in these highly functionalized copolymers. Molecular reagents such as water and amines (even the highly reactive stannylamines) do not react with the copolymers. This is in contrast to the behavior of the simple cyclic phosphazenes as was noted in the introduction and may be indicative of entanglement of the phosphazene in the random coil of the copolymer chain. Strongly anionic reagents such as NaOR (R=CH_3, C_2H_5, CH_2CF_3, C_6H_5) or $NaNH_2$ will effect complete substitution of the phosphorus-fluorine bonds. These results demonstrate the ability to effect wide variations in copolymer properties by taking advantage of the polyfunctional nature of the cyclophosphazene substituents.

Determination of molecular weights was accomplished via gel permeation chromatography (GPC) with selected samples checked using absolute methods (membrane osmometry for $\bar{M}_n$ and equilibrium ultracentrifugation for $\bar{M}_w$). The GPC

experiments show a normal distribution with no evidence of bimodal character.
Values for molecular weights of around 100,000 are observed for copolymers with
low phosphazene content and appear to approach 25,000 as a limit for copolymers
with high phosphazene content. This behavior strongly suggests that the propenyl-
phosphazene is involved in chain transfer and/or termination. Crude values of
reactivity ratios were determined and used to calculate Alfrey-Price Q and e
parameters. These data indicate that the olefinic center is highly polar and with-
out significant resonance stabilization. This model for the electronic structure
of an organic π-electron system bonded to a phosphazene ring is consistent with the
results of our spectroscopic invistigations of organophosphazenes. The ^{13}C NMR
data on 1 indicates a highly polar olefin. UV photoelectron spectroscopy studies
of aryl phosphazenes show that the phosphazene acts as a strong electron with-
drawing substituent but does not enter into significant mesomeric interactions with
the aryl π-system [14]. These results allow us to gain a clear understanding of
some of the difficulties encountered in the preparation and polymerization of 1.

The synthesis of 1 is hampered by the oily by product referred to above.
These by products can be partially fractionated. The mass spectrum of the lowest
viscosity sample shows a mass greater than 1 but less than required for two $N_3P_3F_5$
units. Molecular weights of medium viscosity fractions are around 1000 [15]. NMR
studies of medium and high viscosity samples show evidence for carbon atoms bound
to two phosphorus centers and for a geminal $N_3P_3F_4R_2$ unit. Based on these results, one
can envision attack of propenyl lithium on the highly polar olefinic center in 1.
This process can continue or the resulting anionic species can displace a fluorine
atom on another molecule of 1 thus leading to the types of materials observed as
by products. In the polymerization studies, the radical formed from 1 will be
highly polar and without significant resonance stabilization consequently it will
be a very reactive entity. This reactivity will result in a tendency towards chain
transfer or other termination modes hence the molecular weight decrease with increased

phosphazene content. The reactive propenylphosphazene radical will prefer to add to a monomer which will form a stable radical (i.e. styrene); consequently one observes copolymer compositions rich in styrene.

NEW ORGANOFUNCTIONAL PHOSPHAZENES

Based on the results we obtained in the study of the propenylphosphazene system, we have set three major goals for our continued work in this area. These goals are: synthesis of less polar olefinic phosphazenes; (thus allowing for a broad range of incorporation) development of new types of organofunctional units on the phosphazene ring; development of less expensive monomers.

The first problem which we felt we had to deal with was olefin polarity. The ramifications of a highly polar olefin were described in the preceeding section. We reasoned that one could counter balance the electron withdrawing effect of the phosphazene by dealing with olefins with *strongly electron donating* substituents. We chose the electron rich vinylethers as our example of this class of compounds. The vinylethers can be metalated in a facile manner by treatment with tert-butyl lithium to yield 1-lithioalkoxyethylenes. The lithium reagents were allowed to react with $N_3P_3F_6$ to produce the appropriate substituted phosphazene [15]. Our premise of potentially reduced polarity was born out in the synthetic studies.

$$N_3P_3F_6 + LiC(OR)=CH_2 \longrightarrow N_3P_3F_5C(OR)=CH_2$$
$$R = CH_3(2); \ C_2H_5(3)$$

$$N_3P_3F_6 + 2LiC(OR)=CH_2 \longrightarrow 2,2-N_3P_3F_4\{C(OR)=CH_2\}_2$$
$$R = CH_3, \ C_2H_5$$
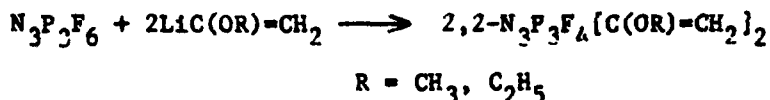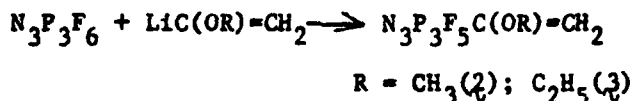
We did not observe any of the oily by products resulting from degradation via anionic attack on the olefin which occurred in the propenyl system. In further contrast to the propenyl system, we could obtain disubstituted derivatives. The reaction follows a geminal pathway at the stage of disubstitution. Attempts to introduce additional substitution did bring on degradation reactions but preliminary

evidence indicates that the degradation proceeds by displacement of an alkoxy function rather than attack on the carbon-carbon double bond. We have further evidence for the reduction of polarity in the olefinic centers of $\mathcal{2}$ and $\mathcal{3}$ over $\mathcal{1}$ in that there is a change in the olefinic methylene ^{13}C NMR chemical shift of over 30 ppm on going from the propenyl to the vinylether system. The ^{13}C NMR shifts in $\mathcal{2}$ and $\mathcal{3}$ are representative of an olefin with a weak electron withdrawing substituent; i.e. the polarity of $\mathcal{2}$ or $\mathcal{3}$ is comparable to vinyl acetate. Thus, we have attained our goal of reduction of olefin polarity and as an added benefit the organic starting material for the synthesis of $\mathcal{3}$ is substantially less expensive than is the case in the synthesis of $\mathcal{1}$.

Having a new, promising monomer, $\mathcal{3}$, we are proceeding to examine its behavior in copolymerization reactions. The radical copolymerization of $\mathcal{3}$ with styrene takes place smoothly to give a series of copolymers which exhibit flame retardancy and a broad range of solubility as was found in the propenylphosphazene/styrene copolymers.

$$\mathcal{3} + C_6H_5CH=CH_2 \longrightarrow +(\underset{C_6H_5}{CHCH_2})(\underset{N_3P_3F_5}{C(OC_2H_5)CH_2})_x]_n$$
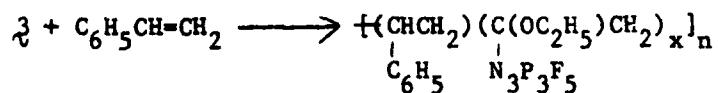
$$x = 0.04 \text{ to } 0.77$$

One observes significantly higher levels of incorporation of $\mathcal{3}$ into the copolymer compared to $\mathcal{1}$ under similar conditions (x = 0.77 vs 0.58). Thus the effect of reduced olefin polarity which was manifested in the synthesis and spectroscopy of $\mathcal{2}$ and $\mathcal{3}$ also is noted in the copolymer synthesis, i.e., there is apparently less chain termination and/or transfer with the less polar olefinic phosphazene. Reactivity ratios were calculated using both the traditional Finemann-Ross (r_1 (styrene) = 3.40; $r_2(\mathcal{3})$ = 0.30) and the improved Kelen-Tudos [1] (r_1 = 3.56; r_2 = 0.28) procedures. Reasonable qualitative agreement was obtained between the two linearization methods. The $r_1 \cdot r_2$ product is close to one, indicating that we are dealing with an ideal copolymerization system. A comparison of the reactivity ratios for ethylvinyl ether and $\mathcal{3}$ in styrene copolymerization is striking. In the former system, the values are

$r_1 = 80$ (ethylvinyl ether) and $r_2 = 0$ (styrene). Clearly, the phosphazene has effected a significant modification of the reactivity of the vinylether. The origin of this modification can be traced to the polarity changes previously discussed and the increased steric requirements of 3. The net result is that 3 doesn't behave as a typical vinyl ether e.g. it does not undergo cationic polymerization.
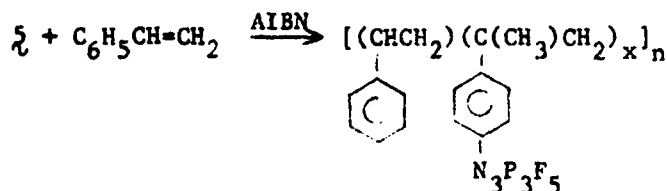
In our search for phosphazene based monomers exhibiting a broad spectrum of reactivity with a wide range of organic monomers, we are examining the phosphazene substituted styrenes. The meta (4) and para (5) α-methylstyrene derivatives are conveniently prepared via the organolithium route. Copolymerization of 5 with styrene

$$Br-\langle\!\langle C \rangle\!\rangle_{C(CH_3)=CH_2} + 2Li \longrightarrow Li \cdot C\langle_{C(CH_3)=CH_2} \xrightarrow{N_3P_3F_6} N_3P_3F_5-\langle\!\langle C \rangle\!\rangle_{C(CH_3)=CH_2}$$
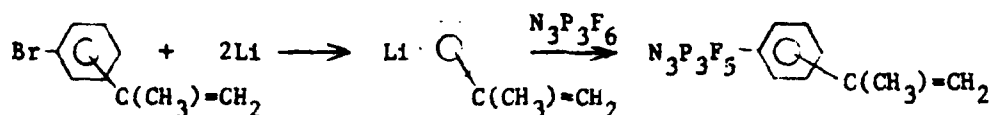
yields copolymers with the highest degree of phosphazene incorporation to date. Equivalent reactions with the meta α-methylstrene derivative (4) give significantly

$$5 + C_6H_5CH=CH_2 \xrightarrow{AIBN} [(CHCH_2)(C(CH_3)CH_2)_x]_n$$

$$\underset{}{\bigcirc_C} \quad \underset{N_3P_3F_5}{\bigcirc_C}$$

$$x = \text{to } 0.86$$

lower levels of incorporation. It will be of interest to determine if, in addition to the expected steric barrier, in 4 , there is an electronic component preferentially operative in one of the isomers. We are planning to prepare homopolymers with a high concentration of pentafluorophosphazene units on the surface. One route to these materials would be from the styrene analogs of 4 and 5. The tendancy to anionic initiation of bromostyrenes by lithium reagents has forced us to seek synthetic routes involving protected olefinic centers. Work on this problem is continuing and it will be of interest to determine if there are any electronic

barriers to homopolymerization in these materials.

In an attempt to prepare new types of organofunctional phosphazenes, we have recently begun to look at alkynlphosphazenes. Some years ago Chivers showed that the lithium reagent derived from phenylacetyene undergoes reactions with $N_3P_3F_6$ leading the mono (6) and geminally disubstituted (7) fluorophosphazene derivatives [17]. We have examined the organofunctional nature of 6 in metal carbonyl catalyzed

$$N_3P_3F_6 + nLiC\equiv CC_6H_5 \longrightarrow N_3P_3F_{6-n}(C\equiv CC_6H_5)_n$$
$$n = 1,2$$
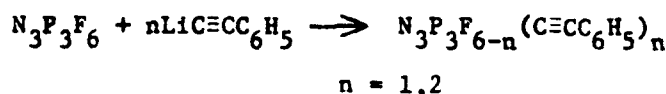
cyclooligiomerization reactions.

+
other isomers
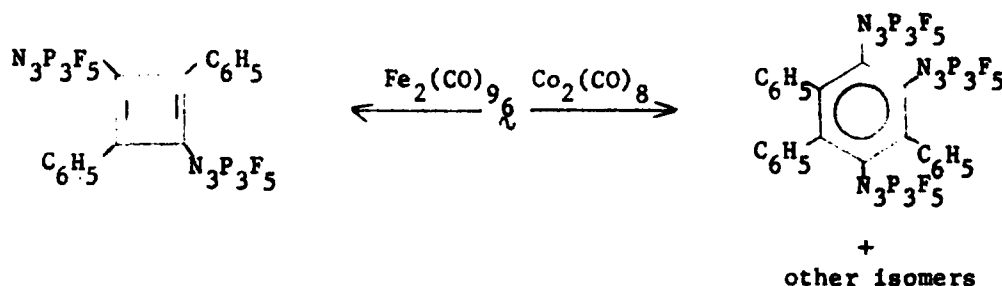
In order to have a more facile entry into polymer systems, we set out to prepare phosphazenes with terminal acetylene substituents. This was accomplished by the use of the trimethylsilyl protecting group which could be removed by treatment with the fluoride ion. There are several points of interest in the chemistry

$$N_3P_3F_6 + nLiC\equiv CSi(CH_3)_3 \longrightarrow N_3P_3F_{6-n}(C\equiv CSi(CH_3)_3)_n$$
$$n = 1,2$$

$$N_3P_3F_{6-n}(C\equiv CSi(CH_3)_3)_n \xrightarrow[C_2H_5OH]{NaF} N_3P_3F_{4-n}(OC_2H_5)_2(C\equiv CH)_n$$
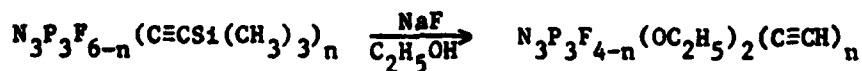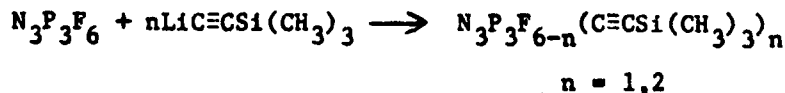
described in these synthetic sequences. The substitution pattern in the lithio trimethylsilylacetylene reaction is predominantly non-geminal (in contrast to the geminal route favored by lithio phenylacetylene). The displacement of the trimethylsilyl group is accompanied by the addition of two ethoxide functions

to the phosphazene ring. The monoacetylene derivative undergoes radical co-
polymerization with styrene to give copolymers with mixed saturated and unsaturated

$$2,4,6-N_3P_3F_3(OC_2H_5)_2C \equiv CH + C_6H_5CH=CH_2 \longrightarrow \begin{bmatrix} (CHCH_2) \\ | \\ C_6H_5 \end{bmatrix} \begin{matrix} (CH=CH)_x \\ | \\ N_3P_3F_3(OC_2H_5)_2 \end{matrix} \end{bmatrix}_n$$
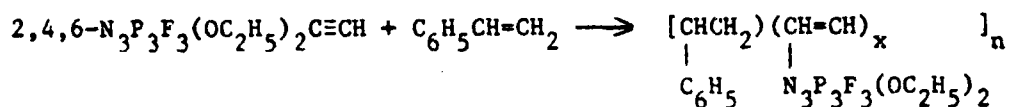
units in the backbone chain.

Our initial exposure to the alkynlphosphazenes suggests the possibility of
a rich monomer and polymer chemistry which can be derived from this new class of
organofunctional phosphazenes. Two of our immediate goals in this area are
to investigate homopolymerization of alkynlphosphazenes and explore the non-geminal
derivatives as potential cross-linking reagents.

Up to this point, all of our examples have involved organofunctional
phosphazenes with phosphorus-carbon bonds. While these systems have many advantages,
particularily in terms of thermal stability, there are also some disadvantages.
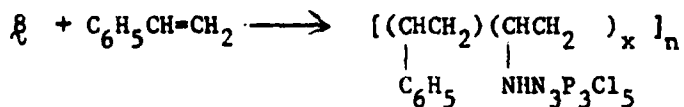Often reoccurring problems with the aforementioned systems include the cost and
extra synthetic steps involved in dealing with $N_3P_3F_6$ rather than the commercially
available hexachlorocyclotriphosphazene, $N_3P_3Cl_6$. The strong electron withdrawing
effect of the phosphazene is experienced directly when the olefinic center is
directly bonded to a ring phosphorus atom. In order to try to circumvent these
difficulties, we have examined olefins which are insulated from the phosphazene by
a heteroatom such as nitrogen or oxygen. These materials can usually be prepared
directly from $N_3P_3Cl_6$.

Our first, and somewhat abortive, attempts involved allylamines. Allcock has
shown that the treatment of hexa(allylamino)cyclotriphosphazene, $N_3P_3(NHCH_2CH=CH_2)_6$,
with radical initiators yield a hard, insolubly cross-linked material [18]. We
prepared the monoallylamino derivative of $N_3P_3Cl_6$ and carried out copolymerization

reactions with styrene. We could only get a maximum of six percent phosphazene

$$N_3P_3Cl_6 + H_2NCH_2CH=CH_2 \longrightarrow N_3P_3Cl_5NHCH_2CH=CH_2 \quad (8)$$

$$8 + C_6H_5CH=CH_2 \longrightarrow \left[(CHCH_2)(CHCH_2)_x \right]_n$$
$$\begin{array}{cc} | & | \\ C_6H_5 & NHN_3P_3Cl_5 \end{array}$$

incorporation. Attempts at homopolymerization of the derivative of diallylamine, $N_3P_3Cl_5N(CH_2CH=CH_2)_2$, appeared to give oligiomeric materials possibly by a cyclopolymerization reaction. The autoinhibitory effect of allylic monomers poses a significant barrier to further development of these monomers.

Undaunted by these results, we have recently produced an extremely exciting series of monomers from the reactions of enolate anions with the halophosphazenes. The enolate anion of acetaldehyde can be prepared quantitatively by the reaction of butyllithium with tetrahydrofuran. We have shown that this ambident nucleophile undergoes reaction at the oxygen atom to yield vinyloxycyclophosphazenes [19].

$$N_3P_3X_6 + O\overset{}{\diagdown}CH_2 \longrightarrow N_3P_3X_5OCH=CH_2$$
$$Li^+$$
$$X=F(9); =Cl(10)$$
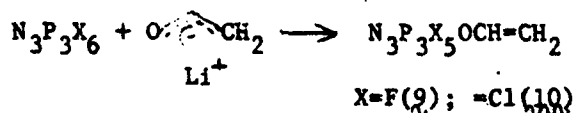
Recently, we have also prepared a butadienyloxy derivative. There is a broad range

$$(CH_3)_3SiO\diagdown\diagdown \xrightarrow{n-C_4H_9Li} O\diagdown\diagdown \xrightarrow{N_3P_3Cl_6} N_3P_3Cl_5O\diagdown\diagup$$
$$Li^+$$
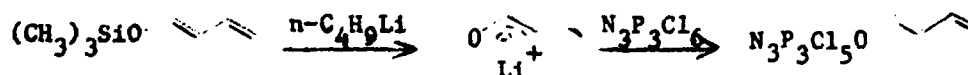
of new and inexpensive (relative to other organophosphazenes) potential monomers available via these routes. We have examined the halophosphazene/enolate anion reaction in detail.

$$N_3P_3X_6 + nLiOCH=CH_2 \longrightarrow N_3P_3X_{6-n}(OCH=CH_2)_n$$
$$x=F,Cl; n=1-6$$
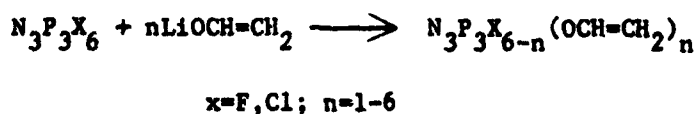
In the chloro derivatives, $N_3P_3Cl_{6-n}(OCH=CH_2)_n$, we have ^{31}P NMR evidence for the existance of all possible geometrical isomers in the series. The non-geminal

isomers predominate (non-geminal:geminal = 96:4). We have determined the composition

of isomeric mixtures by computer simulation of each component and weighting each

component in such a way as to reproduce the mixture spectrum. The fluoro series,

$N_3P_3F_{6-n}(OCH=CH_2)_n$, contains only the non-geminal isomers. In addition to the

polymer chemistry of the monosubstituted derivatives 9 and 10, we are excited about

the possibility of using the non-geminal disubstituted derivatives as chain

branching and cross-linking monomers and the non-geminal trisubstituted materials

as precursors to star polymers.

We started our polymerization studies by examining the reactions of 10 with

various organic monomers to give a large number of new types of flame retardant

$$[(CHCH_2)(CHCH_2)_x]_n$$
$$|\qquad\qquad|$$
$$C_6H_5\qquad ON_3P_3Cl_5$$
$$\uparrow$$

$[(C(CH_3)CH_2)(CHCH_2)_x]_n \longleftarrow$ 10 $\longrightarrow [(CHCH_2)(CHCH_2)_x]_n$

$[(C(CH_3)CH_2)(CHCH_2)_x]_n$ $CH_3OCC(CH_3)=CH_2$ $CH_3COCH=CH_2$ $[(CHCH_2)(CHCH_2)_x]_n$
COCH_3   ON_3P_3Cl_5   O   O   OCCH_3   ON_3P_3Cl_5
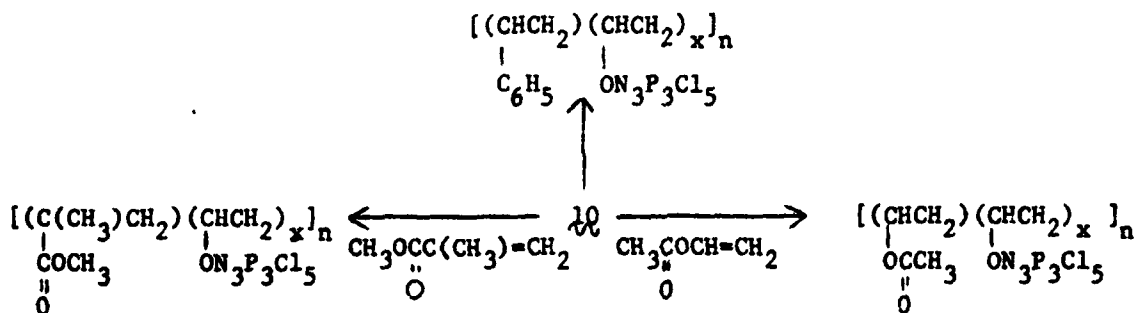
copolymers. Two features of this study are worthy of comment. The first of these

is the broad range of organic monomers which can combine with the phosphazene.

Secondly, in the methylmethacrylate system, we can easily obtain greater than

1:1 ratios of 10 to methylmethacrylate in the copolymer. This is the first of

our organofunctional phosphazenes in which the phosphazene becomes the predominant

comonomer. This observation demonstrates that one can affix two (or more) olefinic

phosphazenes together in a copolymer and suggests the possibility of homopolymerization

of 10.

In our first attempts at homopolymerization of 10, we used benzoyl peroxide

as the radical initiator and obtained a black, sponge like insoluble solid with

an approximate elemental analysis of $[N_3P_3Cl_4OCHCH_2]$. This implies radical reactions

at both phosphorus-chlorine and carbon-carbon bonds leading to a highly cross-linked material. However, when AIBN is used as the initiator, the polymerization proceeds smoothly and rapidly to give a polymer with a number average molecular

$$[N_3P_3Cl_4OCHCH_2]_n \xleftarrow{\text{C}_6\text{H}_5\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OO}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{C}_6\text{H}_5} \underset{10}{} \xrightarrow{\text{AIBN}} \begin{array}{c}(\text{CHCH}_2)_n \\ | \\ \text{ON}_3\text{P}_3\text{Cl}_5 \end{array} \quad (11)$$
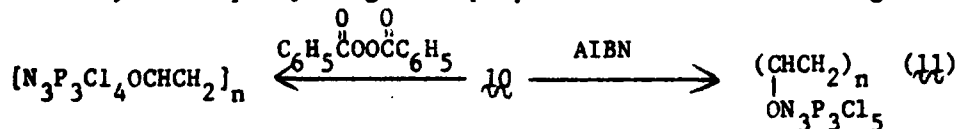
weight (determined osmometrically) of 285,000. The new polymer (11) exhibits flame retardancy, good solubility in a number of solvents and can be cast into flexible films. This unique polymer presents an interesting structural "inversion" over traditional inorganic polymers such as polysiloxanes and polyphosphazenes. In the classical case, the inorganic backbone is surrounded by a protective sheath of organic substituents. In 11, the organic backbone is surrounded by inorganic rings. The fact that there is one $N_3P_3Cl_5$ moiety per monomer unit means that 11 is a highly functionalized polymer. Consequently, one can employ the numerous reactions of cyclophosphazene chemistry [4,5] to effect chemical modication of the composition and properties of 11. We have demonstrated the possibility of such a transformation by carrying out the reaction of 11 with dimethylamine to yield the totally dimethylaminated derivative of 11.

$$11 + 5_n(\text{CH}_3)_2\text{NH} \longrightarrow \begin{array}{c}(\text{CHCH}_2)_n \\ | \\ \text{ON}_3\text{P}_3[\text{N}(\text{CH}_3)_2]_5 \end{array}$$

The monomers such as 10 which are derived from enolate anions appear to satisfy most of the basic goals which we have set for an ideal organofunctional phosphazene i.e. reduced polarity (broader reactivity), new types of functional units and reduced expense. The range of chemical and physical investigations available to us in the study of these systems will allow for the production of a considerable amount of new and exciting phosphazene chemistry.

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